

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) December 2013		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To) October 2013- December 2013
4. TITLE AND SUBTITLE Molecular Orbital Based Design Guidelines for Hypergolic Energetic Ionic			5a. CONTRACT NUMBER FA9300-11-C-3004	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) D. Sengupta and G. L. Vaghjiani			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER 300511VQ	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB, CA, 93524-7680			8. PERFORMING ORGANIZATION REPORT NO.	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Dr. Edwards AFB, CA, 93524-7048			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RQ-ED-JA-2013-243	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES Journal article published in the Angewandte Chemie, Vol. 40, 2015. PA Case Number: 13543; Clearance Date: 02 Dec 2013. © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.				
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15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
c. REPORT	b. ABSTRACT	c. THIS PAGE		
Unclassified	Unclassified	Unclassified	SAR	7
				19a. NAME OF RESPONSIBLE PERSON G. Vaghjiani
				19b. TELEPHONE NO (include area code) 661-525-5657

# Molecular Orbital Based Design Guideline for Hypergolic Ionic Liquids

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**Abstract:** Currently, monomethyl hydrazine is the most widely used hypergolic rocket fuel. Due to its high toxic vapor, there is a thrust towards developing low-toxic hypergolic fuels. Ultra-low vapor pressure ionic liquids are one such potential category of fuels. However, designing ionic liquid with ignition delay comparable to monomethyl hydrazine is a challenge, because fundamental understanding of the hypergolic nature of ionic liquids is far from clear. This work used the computed energy gap values between the highest occupied molecular orbitals (HOMO) of the anions for a series of ionic liquids and the lowest occupied molecular orbital (LUMO) of  $\text{HNO}_3$ , and variation in the computed relative heats of formation,  $\Delta H_f$ , of these anions

to develop correlations to predict hypergol activity between an ionic liquid fuel and nitric acid as the oxidizer. The observed trends in HOMO–LUMO energy gap and  $\Delta H_f$  values can be used successfully to verify not only hypergolicity of known systems but also the lack of this phenomenon in  $\text{OH}^-$  and  $\text{BF}_4^-$  based ionic liquids. It was shown that through suitable substitution of electron withdrawing or electron donating groups in the anion, the energy gap and the  $\Delta H_f$  values could be tailored into an optimal range that would have a high probability for the new system to exhibit hypergolic reactivity. To validate our method, we suggest herein new ionic liquid structures for synthesis and experimental screening.

**Keywords:** Hypergolic • Molecular orbital • Design guideline • Heat of formation • Energetic ionic liquids

## Introduction


A hypergolic fuel will spontaneously ignite when mixed with a suitable oxidizer. These types of fuels are routinely used as rocket propellants in many space and missile applications. Common oxidizers that may be used are nitrogen tetroxide (NTO) and inhibited red fuming nitric acid (IRFNA). Currently used hypergolic fuels include hydrazine, as well as its derivatives; monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH). These fuels are highly toxic, have high vapor pressures, and are known to be carcinogens. For these reasons, replacements for hydrazines are sought. Ionic liquids (ILs), due to their negligible vapor pressure, are being considered as viable alternatives. Since the recent discovery of dicyanamide (DCA) based hypergolic energetic ionic liquids (EILs) [1], several papers have reported on the synthesis of new hypergolic EILs, which have the potential to provide improved propulsion performance [2–4] compared to the MMH/NTO baseline system. An important challenge is to design hypergolic EILs with short ignition delay (ID) times that are comparable to the ID time for MMH/NTO. Under current practices, EILs are first synthesized without any prior knowledge of their ability of being hypergolic with a suitable oxidizer. A trial-and-error drop test is followed to discern whether the fuel will actually undergo a hypergolic reaction. Therefore, the development of a simple, but reliable design guideline for *a priori* prediction of hypergolic EILs could have a signifi-

cant impact in reducing the time to develop a viable hypergolic EIL propellant.

Although there have been some efforts in the past to understand hypergolic reaction mechanisms and to correlate ID times with molecular properties [5–8], the utility of such schemes has been limited to molecular liquids, since the increased complexity of cations/anions Columbic interactions present in ILs is not required to be considered for molecular liquids. Recently, we reported relationships between ID times and a set of quantum chemically computed descriptors using linear quantitative structure property relationship (QSPR) and artificial neural network (ANN) approaches [9]. The observed correlations were based on charge partial charge surface area (CPSA) based descriptors calculated

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 Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/prop.201400087> or from the author.

from semi-empirical quantum calculations. Chambreau et al. [10] reported Fourier transform infrared experiments and *ab initio* calculations to understand the mechanism of hypergolic reaction of a DCA anion based EIL and nitric acid, and found the underlying reactions to be very complex. We have performed reactive molecular dynamics simulations on an EIL/nitric acid system to understand the fundamental chemical reactions that lead to hypergolic ignition [11] and also observed the reaction chemistry to be complex. Although these studies provide important information regarding the initiation chemistry, there is no guidance available in the literature for *a priori* design of ILs that has a potential to show hypergolicity. Previous experimental observations have concluded that the anion plays an important role in determining the hypergolic tendency of EILs [1,10,12]. Recently, McRay et al. [13] attempted to correlate ID times with molecular structures and thermophysical properties, such as viscosity, thermal conductivity and density. While they found some evidence that ID times depended on the nature of the exocyclic substitution in the five-membered ring cations for dicyanamide-based ILs, no significant correlation was observed with any of the thermophysical properties.

The goal of this work is to obtain a fundamental understanding of the cause of hypergolic reactions based on theoretical principles and provide a guideline for designing hypergolic ionic liquids. In principle, such a guideline may therefore be used by a synthetic chemist at the concept stage for selecting an anion, which would have a high probability for forming a hypergolic fuel. The validity of the present approach is tested against a number of anions that have been reported in the literature.

## Computational Methods

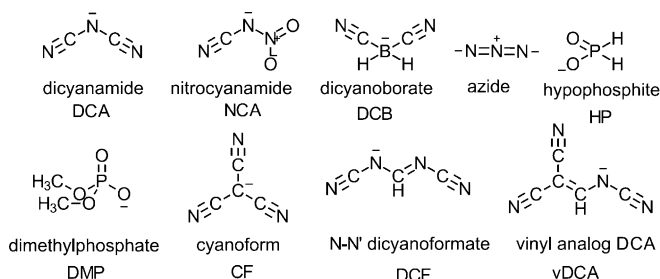
Quantum mechanical calculations were performed using B3LYP exchange correlation functional [14–16] with 6-31++G(d,p) basis set. Diffuse functions were added to obtain a better description of the anions. All heats of formation values,  $\Delta H_f^\circ$ , reported here are calculated at 298.15 K using a highly accurate complete basis set method, CBS-QB3 [17]. The mean absolute deviation of the heats of formation of the method is reported to be 4.98 kJ mol<sup>-1</sup> [18]. All calculations were performed using Gaussian 03 program package [19].

## Results and Discussion

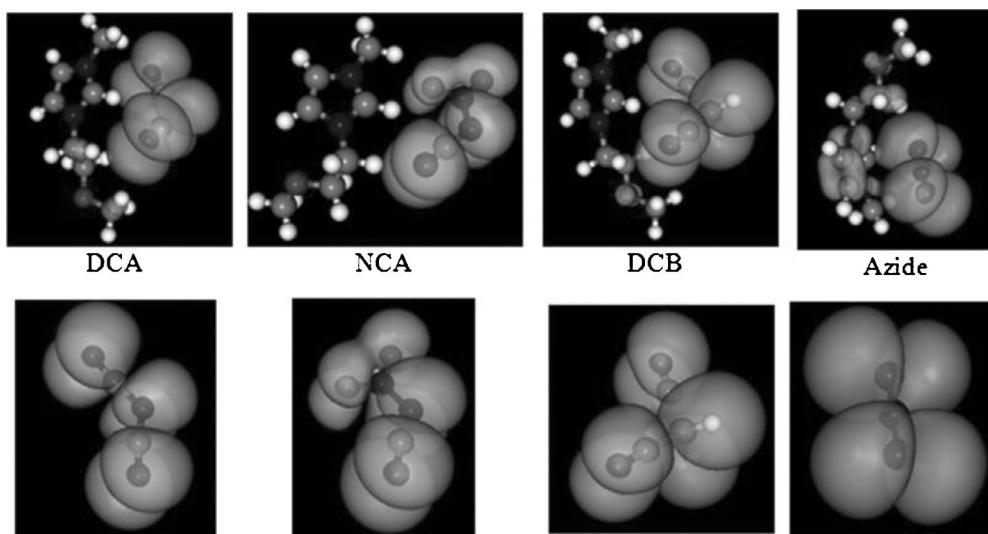
### Importance of the Anion

Figure 1 shows the anions that were experimentally synthesized and the hypergolicity of the EILs containing these was experimentally tested.

Figure 2 shows that the nature of the electron density surface of the HOMO of the cation/anion ion-pair remains unchanged compared to that of the isolated anion, and ac-



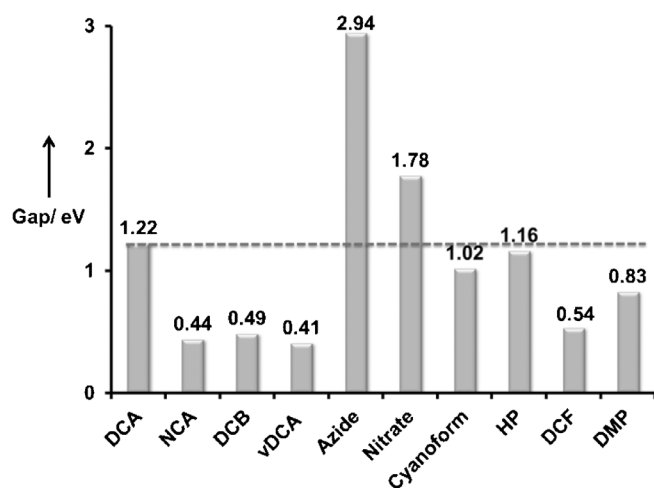
**Figure 1.** Hypergolic EILs, whose ignition delay (ID) times were reported (see for example Refs. [1,11]).



**Figure 2.** HOMO of the ion-pair (upper panel) compared to that of the corresponding isolated anion (lower panel).

cording to frontier molecular orbital (FMO) theory [20], the HOMO of the EIL should be an electron donor, where the reaction between the EIL and the nitric acid can be considered to be of the acid-base type. Previously, this FMO approach has been applied in interpreting reactivity in Diels–Alder reactions, photochemical reactions, and organometallic reactions [21–23].

According to the molecular orbital representation of the acid-base theory, the interaction between the acid and the base is dictated by the “energy gap” between the HOMO of the anion and LUMO of  $\text{HNO}_3$ , and this quantity can be explored as a criterion for hypergolicity (or reactivity). While it is mathematically complex to construct an accurate interaction matrix element of the orbital interaction, it is known from perturbation theory that the orbital interaction is dictated by the energy gap between orbitals [24]; the smaller the gap, the larger the interaction. Figure 3 shows the



**Figure 3.** Computed “energy gap” for various experimentally studied anions (see Tables S1 and S2, Supporting Information, for the corresponding heat of formation and ionization potential values).

energy gap values for the anions studied herein and for which experimental hypergolicity is known. DCA based hypergolic EILs have received the greatest attention in the literature following the first discovery of an IL hypergol [1,12]. Therefore, here we consider DCA as the baseline system (horizontal line in Figure 3). Any anion with an energy gap that falls in the vicinity or below this line is predicted to be hypergolic when coupled with an appropriate cation provided it meets the heat of formation criterion (as discussed later).

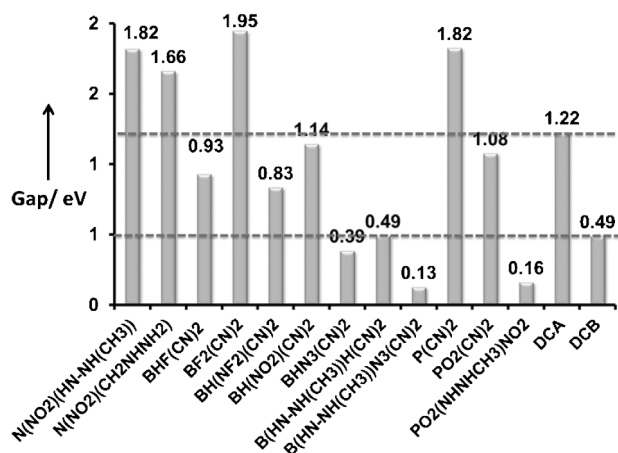
One of the most striking features is the difference in the “energy gap” values of azide and DCB. Azide ILs reported in the literature were found to be non-hypergolic, except for two examples [12]. On the other hand, DCB containing EILs have been found to be hypergolic. EILs containing NCA were also found to be hypergolic.  $\text{NO}_3^-$  has a higher “energy gap” than DCA and is predicted to be non-hyper-

golic. In fact, so far only one IL containing  $\text{NO}_3^-$  was found to be hypergolic. Recently, a few EILs containing the  $\text{H}_2\text{PO}_2^-$  (HP) anion have been synthesized by the Shreeve group [25]. The majority of them were found to be hypergolic, however, they had longer ID times. Also, out of two synthesized DCF containing EILs, one of them was found to be hypergolic. While there are many reports of EILs containing NCA, DCA, DCB, and azide in the literature, more  $\text{H}_2\text{PO}_2^-$  and DCF containing EILs should be synthesized to further validate our probabilistic approach for identifying EIL hypergols.

DMP is one anion that has a lower “energy gap”, but the only DMP EIL so far synthesized has been found to be non-hypergolic. Similarly, two other anions, vinyl analogue of DCA (i.e., vDCA) and CF [cyanoform,  $\text{C}(\text{CN})_3^-$ ] are also predicted to be hypergolic, but the synthesized EILs containing these two anions were also found to be non-hypergolic. A close look at the structures of the anions reveals that, unlike other anions, both vDCA and CF contain C–C bonds. The structural difference of these two anions from others could lead to differences in the reactivity that is not captured in the simple interpretation described above. Therefore, more theoretical and experimental work needs to be performed to isolate the effect of C–C bond(s) over C–N bond(s). Although it has been shown that the nature of the electron density surface of the HOMO of the cation/anion ion-pair remains unchanged compared to that of the isolated anion, it is worth discussing the effect of the cation on the “energy gap”. In the ion-pair system, there is no covalent bond and therefore orbital mixing is negligible. However, orbital energies of anions are significantly affected by the electrostatic field created by the positively charged cation (and vice versa). This electrostatic effect results in stabilization of the anion HOMO. Our calculations show that for a variety of cations, the magnitude of this stabilization is near identical for a particular anion and that the HOMO energy levels of the ion-pairs are virtually independent of the nature of the cations. Table S4 (Supporting Information) shows the variance in HOMO energy level is below 0.04 eV for the azide anion. Since the LUMO of the  $\text{HNO}_3$  is constant, one could calibrate the “energy gap” to arrive at a new rule. However, obtaining optimized ion-pair structures is a non-trivial task due to the non-bonded interactions, and therefore this work has primarily focused just on the HOMO of the anions.

### Anion Design Guideline

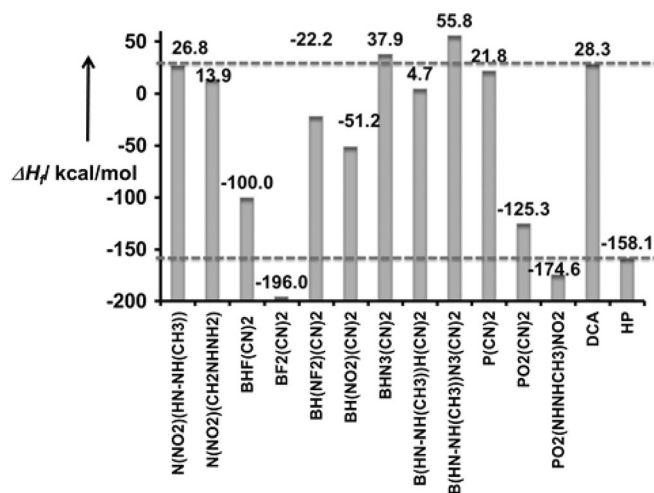
Based on the theoretical ideas discussed above, the anion appears to play an important role in EIL hypergolicity. The interpretation is based on the energies of the HOMO of anions relative to the LUMO of the oxidizer. In principle, one can engineer the HOMO energy of an anion by substitution of a parent anion with different functional groups. It is known that electron withdrawing groups lower the HOMO energy, while electron donating groups elevate the



**Figure 4.** Values of the energy gap for some conceptual anions. DCA and DCB are also shown for comparison.

energy. Therefore,  $-F$ ,  $-NO_2$ , and  $-CN$  will lower, and alkyl, amino, and substituted amino will elevate the HOMO energy compared to its unsubstituted analogue. Since a hypergolic reaction ultimately releases a large amount of heat, the energy content of the anion must also be taken into account in the design strategy; *substitution should be carried out in such a way that does not reduce the energy content (i.e., the  $\Delta H_f$ ) of the new anion drastically compared to that of the parent anion.* Figure 4 shows some conceptual anions and the energy gaps between their HOMOs and the LUMO of the  $HNO_3$ . Their  $\Delta H_f$  values are depicted in Figure 5.

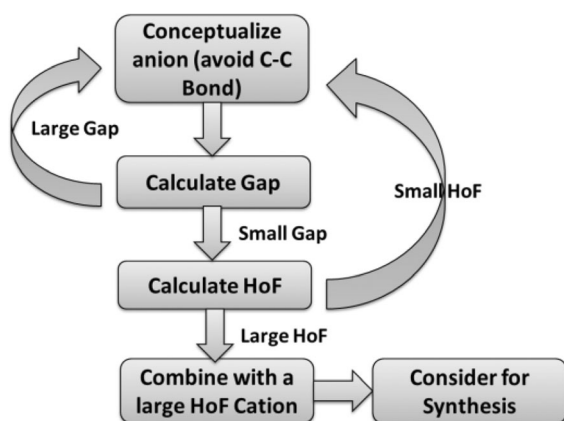
Important observations to note (see Table S3, Supporting Information) include the following: substituting one H in DCB by  $-NO_2$ , reduces its  $\Delta H_f$  from  $-61.5 \text{ kJ mol}^{-1}$  to  $-214.4 \text{ kJ mol}^{-1}$ , while a  $-F$  substituted DCB has  $\Delta H_f$  of  $-418.68 \text{ kJ mol}^{-1}$ . Also,  $-NO_2$  brings the HOMO energy of the anion closer to the LUMO than does  $-F$ . Therefore,  $-NO_2$  may be preferable to  $-F$ , if a lowering of anion HOMO is required. If all four groups of DCB are replaced by  $-F$ , the HOMO of the resulting  $BF_4^-$  becomes much lower than LUMO of  $HNO_3$  resulting in a larger absolute gap than with DCA (i.e., 1.54 eV). Moreover, its  $\Delta H_f$  is drastically reduced (i.e.,  $-1728.3 \text{ kJ mol}^{-1}$ ). Therefore the present theory predicts  $BF_4^-$  is unlikely to be hypergolic. Indeed,  $BF_4^-$  containing ionic liquids are found to be very stable, non-energetic, and non-hypergolic. Therefore, a trade-off between the “energy gap” value and the change in  $\Delta H_f$  should be considered during any substitution strategy. So far in the literature, HP (with energy gap similar to DCA) is the lowest  $\Delta H_f$  anion ( $-661.9 \text{ kJ mol}^{-1}$ ) for which EIL hypergolicity was observed. Using this  $\Delta H_f$  anion value as another baseline limit, we see that the  $\Delta H_f$  of DMP of  $-1128.4 \text{ kJ mol}^{-1}$  is far below this limit and has a greater influence than its low “energy gap” of Figure 2, which makes this IL non-hypergolic. New EILs containing DMP should be synthesized and tested for hypergolicity.



**Figure 5.**  $\Delta H_f$  values of some conceptual anions. DCA and HP, respectively, have highest and lowest values of anion  $\Delta H_f$ , for which EIL hypergolicity is experimentally observed.

Promising conceptual anions could be formed via a substitution of one of the H's of DCB by  $-N_3$ . Single substitution would slightly elevate the HOMO of the DCB, but the computed  $\Delta H_f$  increases drastically, from  $-61.5$  to  $158.7 \text{ kJ mol}^{-1}$ . Substitution of the second H by the electron donating  $-N(H)NH(CH_3)$ , which is derived from MMH, would elevate the DCB HOMO, but would still remain below the baseline value of DCA. The computed  $\Delta H_f$ , however, would increase to  $233.6 \text{ kJ mol}^{-1}$ . The other example is the substitution of one  $-CN$  group of DCA by  $-NO_2$ . EILs with this anion (NCA) have been studied and in many cases found to be hypergolic [3]. This substitution brings the HOMO closer to  $HNO_3$  LUMO with an acceptable reduction of  $\Delta H_f$  (from  $118.5 \text{ kJ mol}^{-1}$  for DCA to  $-27.2 \text{ kJ mol}^{-1}$  for NCA). For the  $OH^-$  anion, our calculations show that the value of the “energy gap” is 4.54 eV, which is much higher than that of the azide anion, and with  $\Delta H_f$  of  $-130.2 \text{ kJ mol}^{-1}$ . Clearly  $OH^-$  anion based EILs are unlikely to be hypergolic.

Finally, based on the above computational results and validations, we provide simple rules for designing anions (see Figure 6 above): (1) Conceptualize a preliminary structure for an anion avoiding any C–C bonds; (2) compute its  $\Delta H_f$ ; (3) calculate the “energy gap”, i.e., the difference in energies of anion HOMO and LUMO of  $HNO_3$ ; (4) compare with the baseline value (i.e. of DCA) and adjust this energy difference by functional group substitution, keeping the anion  $\Delta H_f$  in the vicinity of other hypergolic anions known experimentally; and (5) combine the anion with a high energy content cation to make a hypergolic EIL. It should be noted that the theory presented here does not consider the effect of thermophysical properties and therefore, does not predict properties such as melting points, diffusion coefficients, viscosity, thermal conductivities, and specific heats of the suggested ILs containing the conceptual



**Figure 6.** A flowchart of ionic liquid design guideline for hypergolicity.

anions. These thermophysical properties will control the mixing and heat transfer, and will ultimately affect the ID times for ILs with similar chemical reactivities. In order to take into account these effects, one needs to first compute these properties using other theoretical methods, such as molecular dynamics simulations.

## Conclusions

This work provides a fundamental understanding of hypergolic reaction between energetic ionic liquids and nitric acid by coupling frontier molecular orbital theory and thermochemistry derived from *ab initio* quantum chemistry. A simple theoretical model based on frontier molecular orbital theory was proposed for designing anions. The HOMO of the anion retains its character in the ion-pair and therefore expected to be the dominant reactant. The energy gap between the HOMO of anions and the LUMO of  $\text{HNO}_3$  was used as a parameter for interaction between a base and an acid. The larger the interaction is, the higher is the probability that the EIL will be hypergolic provided it meets the requirement of heat of formation. Several concept anions are proposed here that have the potential to form hypergolic EILs. Several other factors, such as mixing rate of the EIL and the oxidizer, heat transfer rates, reaction kinetics and the chemical influence of the cation are capable of affecting hypergolicity, and the scope of the present design approach could be expanded in the future to fully explore these effects.

**Supporting Information** (see footnote on the first page of this article): Details of the heat of formation and energy gap values.

## Acknowledgments

The US Air Force is acknowledged for financial support under the SBIR Contract # FA9300-11-C-3004. The authors also thank Dr. David Newsome for supplying optimized geometries of the ion-pairs.

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Received: April 9, 2014

Revised: June 11, 2014

Published online: August 11, 2014